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Excess Thermodynamic Functions of Solutions of Alcohols with Saturated Hydrocarbons: Application of the UNIQUAC Equation to the Associated Solution Theory

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Two continuous association models (the KRETSCHMER-WIEBE and the MECKE-KEMPTER types) are combined with the UNIQUAC equation of ABRAMS and PRAUSNITZ to derive expressions for the excess Gibbs free energy and excess enthalpy of alcohol-inert component systems. In data reduction, the structural parameters of pure components are obtained by the method proposed by VERA *et al.* The present theory is successfully applied to the correlation of the excess thermodynamic functions of cycloalkanol-cycloalkane systems. Ternary results predicted from binary parameters are shown to be in good agreement with experimental excess properties for the ethanol-cyclohexane-n-heptane system at 20 °C.

Die von KRETSCHMER-WIEBE und MECKE-KEMPTER entwickelten Modellvorstellungen zur theoretischen Beschreibung der Assoziation von Alkoholen in inerten Lösungsmitteln werden mit der UNIQUAC-Beziehung von ABRAMS und PRAUSNITZ kombiniert. Die Struktur-Parameter der reinen Komponenten werden nach der Methode von VERA *et al.* bestimmt. Die Ergebnisse der Berechnungen von Excess-Thermodynamischen Funktionen auch von binären Mischlösungen *cyclischer* Alkohole in *Cyclo*-Alkanen sind in den Tabellen 3 und 4 zusammengefaßt. Ergebnisse von Berechnungen auch am *ternären* System Äthanol-Cyclohexan-n-Heptan mit Hilfe von Parametern aus binären Systemen sind in guter Übereinstimmung mit experimentellen Daten, (Tabelle 5).

1. Introduction

Many investigators have considered the hydrogen bonding of alcohol molecules, which leads to the formation of linear polymeric alcohol complexes, as a main cause of the large deviation from an ideal solution that alcohol-saturated hydrocarbon solutions show. These approaches are called as chemical solution theories whose characteristic is to use several chemical equilibrium constants to fit experimental data. KRETSCHMER and WIEBE [1] formulated the size effect of the alcohol complexes by using the nonathermal Flory-Huggins equation. RENON and PRAUSNITZ [2] studied the Kretschmer-Wiebe equation to reduce experimental vapor-liquid equilibrium and excess enthalpy data for binary solutions of alcohols and saturated hydrocarbons. WIEHE and BAGLEY [3] derived a Mecke-Kempter type equation based on the athermal Flory-Huggins equation by incorporating the ratio of the molar volume of alcohol to that of hydrocarbon as an adjustable parameter. The Wiehe-Bagley equation can not estimate well the excess enthalpy data. NAGATA [4,5] showed that the physical term (the Scatchard-Hildebrand equation) of the nonathermal Flory-Huggins equation can be replaced by a new two-parameter equation and the resultant equations are more flexible than the previous equation in data reduction. ABRAMS and PRAUSNITZ [6] presented the UNIQUAC (universal quasichemical) equation as the generalization of the theory of GUGGENHEIM [7] to mixtures containing molecules of different size and shape by introducing the local composition concept proposed by WILSON [8], showing that the UNIQUAC equation may be used to represent the properties of polymer solutions. One of the advantages of the UNIQUAC equation is to represent liquid-liquid equilibria for a variety of mixtures.

We discuss here the application of the UNIQUAC equation to associated solutions, because the derived associated solution theory may be used to correlate ternary liquid-liquid equilibrium data for alcohol-nonassociating component systems having an immiscible region between nonassociating components while the equations proposed by NAGATA [4,5] are unable to do so.

2. Theory

According to ABRAMS and PRAUSNITZ [6], the UNIQUAC equation for a multicomponent system is expressed by

$$g^E = g^E \text{ (combinatorial)} + g^E \text{ (residual)} \tag{1}$$

$$g^E \text{ (combinatorial)}/RT = \sum_i x_i \ln (\varphi_i/x_i) + (Z/2) \sum_i q_i x_i \ln (\theta_i/\varphi_i) \quad (2)$$

$$g^E \text{ (residual)}/RT = -\sum_i x_i q_i \ln \left(\sum_j \theta_j \exp \{-(u_{ji} - u_{ii})/RT\} \right) \quad (3)$$

where the average area fraction θ and the average segment fraction φ are defined by

$$\theta_i = q_i x_i / \sum_j q_j x_j \quad (4)$$

$$\varphi_i = r_i x_i / \sum_j r_j x_j \quad (5)$$

where x is the mole fraction, Z is the coordination number equal to 10 and q and r are pure component structural parameters. Eq. (3) shows that there are two adjustable parameters per binary.

Excess Gibbs Free Energy

A refers to the alcohol (component 1) and 2 and 3 stand for inert components. Continuously associated solution models are based on the following fundamental assumptions:

1. The alcohol forms linear hydrogen-bonded polymers by consecutive chemical reactions of the type $A_1 + A_{i-1} = A_i$.

2. The segment number of an alcohol i-mer A_i is given by that of a monomer multiplied by the degree of polymerization i.

3. Both chemical and physical contributions are responsible for deviations from an ideal solution of alcohols and saturated hydrocarbons.

The previous approaches have shown that the chemical contribution term is concerned with the combinatorial term of the Gibbs free energy of mixing, which is obtained from Eq. (2)

$$g^M \text{ (combinatorial)}/RT = \sum_i^{\infty} n_{A_i} \ln \varphi_{A_i} + n_2 \ln \varphi_2 + n_3 \ln \varphi_3 + (Z/2) \left[\sum_i^{\infty} q_{A_i} n_{A_i} \ln (\theta_{A_i}/\varphi_{A_i}) + q_2 n_2 \ln (\theta_2/\varphi_2) + q_3 n_3 \ln (\theta_3/\varphi_3) \right] \quad (6)$$

where n is the mole number of chemical species.

The chemical potentials are obtained by differentiating Eq. (6) with respect to the number of moles of each chemical species.

$$\Delta\bar{g}_{A_i} = RT\Big[\ln\varphi_{A_i} + (Z/2)\,q_{A_i}\ln(\theta_{A_i}/\varphi_{A_i}) + \sum_j^{\infty}\varphi_{A_j}(l_{A_i} - r_{A_i}\,l_{A_j}/r_{A_j}) + \varphi_2\,(l_{A_i} - r_{A_i}\,l_2/r_2) + \varphi_3\,(l_{A_i} - r_{A_i}\,l_3/r_3)\Big] \tag{7}$$

where l is called the bulk factor [9] and it is defined by

$$l = (Z/2)\,(r - g) - r + 1\,. \tag{8}$$

PRIGOGINE and DEFAY [10] showed that the chemical potential of stoichiometric component 1 is equal to that of the monomer of the same component in the associated solution.

$$\Delta\bar{g}_{A_1} = RT\Big[\ln\varphi_{A_1} + (Z/2)\,q_{A_1}\ln(\theta_{A_1}/\varphi_{A_1}) + \sum_j^{\infty}\varphi_{A_j}(l_{A_1} - r_{A_1}\,l_{A_j}/r_{A_j}) + \varphi_2\,(l_{A_1} - r_{A_1}\,l_2/r_2) + \varphi_3\,(l_{A_1} - r_{A_1}\,l_3/r_3)\Big]. \tag{9}$$

We take the pure alcohol as a new reference state.

$$\Delta\bar{g}^{\circ}_{A_1} = RT\Big[\ln\varphi^{\circ}_{A_1} + (Z/2)\,q_{A_1}\ln(\theta^{\circ}_{A_1}/\varphi^{\circ}_{A_1}) + \sum_j^{\infty}\varphi^{\circ}_{A_j}(l_1 - r_1\,l_{A_j}/r_{A_j})\Big]. \tag{10}$$

The chemical potential of alcohol with the new reference state is derived by subtracting Eq. (10) from Eq. (9)

$$\Delta\bar{g}^{E}_{A_1} = \Delta\bar{g}_{A_1} - \Delta\bar{g}^{\circ}_{A_1} = RT\Big[\ln(\varphi_{A_1}/\varphi^{\circ}_{A_1}) + (Z/2)\,q_1\ln(\theta_{A_1}\varphi^{\circ}_{A_1}/\varphi_{A_1}\theta^{\circ}_{A_1}) + \sum_j^{\infty}\varphi_{A_j}(l_1 - r_1\,l_{A_j}/r_{A_j}) + \varphi_2\,(l_1 - r_1\,l_2/r_2) + \varphi_3\,(l_1 - r_1\,l_3/r_3) - \sum_j^{\infty}\varphi^{\circ}_{A_j}(l_1 - r_1\,l_{A_j}/r_{A_j})\Big]. \tag{11a}$$

The last four terms on the right hand side of Eq. (11a) are rearranged as shown in Appendix 1. $\theta_{A_1}/\varphi_{A_1} = \theta_1/\varphi_1$ and $\theta^{\circ}_{A_1}/\varphi^{\circ}_{A_1} = 1$ from Eq. (23).

Then, we get

$$\Delta\bar{g}^{E}_{A_1}/RT = \ln(\gamma_1 x_1)_{\text{chem}} = \ln(\varphi_{A_1}/\varphi^{\circ}_{A_1}) + (Z/2)\ln(\theta_1/\varphi_1) + r_1/S^{\circ} - r_1/S + r_1\{(1 - l_1)\,\varphi_1/r_1 + (1 - l_2)\,\varphi_2/r_2 + (1 - l_3)\,\varphi_3/r_3\} + l_1 - 1 \tag{11b}$$

where S is the total segment number of one mole of the solution and S° is the value of S in pure alcohol state.

$$1/S = \sum_j^\infty \varphi_{A_j}/r_{A_j} + \varphi_2/r_2 + \varphi_3/r_3 \tag{12}$$

$$1/S^\circ = \sum_j^\infty \varphi^\circ_{A_j}/r_{A_j}. \tag{13}$$

We may obtain the chemical potentials of the components 2 and 3 without changing the reference state (pure components 2 and 3).

$$\begin{aligned}\Delta\bar{g}_2/RT &= \ln(\gamma_2 x_2)_{\text{chem}} = \ln\varphi_2 + 1 - r_2/\mathrm{S} + (Z/2)q_2 \ln(\theta_2/\varphi_2) \\ &+ r_2\{(1-l_1)\varphi_1/r_1 + (1-l_2)\varphi_2/r_2 + (1-l_3)\varphi_3/r_3\} + l_2 - 1\end{aligned} \tag{14}$$

$$\begin{aligned}\Delta\bar{g}_3/RT &= \ln(\gamma_3 x_3)_{\text{chem}} = \ln\varphi_3 + 1 - r_3/S + (Z/2)q_3 \ln(\theta_3/\varphi_3) \\ &+ r_3\{(1-l_1)\varphi_1/r_1 + (1-l_2)\varphi_2/r_2 + (1-l_3)\varphi_3/r_3\} + l_3 - 1.\end{aligned} \tag{15}$$

Finally, the chemical contribution term is expressed by

$$\begin{aligned}g^E_{\text{chem}}/RT &= x_1 \ln(\varphi_{A_1}/\varphi^\circ_{A_1} x_1) + x_2 \ln(\varphi_2/x_2) + x_3 \ln(\varphi_3/x_3) + x_2 + x_3 \\ &+ x_1 r_1/S^\circ - (x_1 r_1 + x_2 r_2 + x_3 r_3)/S + (Z/2)\sum_i^3 q_i x_i \ln(\theta_i/\varphi_i).\end{aligned} \tag{16}$$

The last term on the right hand side of Eq. (16) includes shape effect and this term does not appear in the previous equations [1—3], provided that the segment fractions correspond to the volume fractions in the latter equations.

For continuous linear associating reactions of alcohol molecules, two models have been proposed. They differ from each other in defining the chemical equilibrium constant: the Kretschmer-Wiebe and the Mecke-Kempter models. The Kretschmer-Wiebe Model. KRETSCHMER and WIEBE [1] suggested the following chemical equilibrium constant given by

$$K^\varphi = (\varphi_{A_i}/\varphi_{A_1}\varphi_{A_{i-1}})(i-1)/i. \tag{17}$$

Then, we may obtain the segment fractions of alcohol monomer in the solution and in pure alcohol.

$$\varphi_{A_1} = [2K^\varphi\varphi_1 + 1 - (1 + 4K^\varphi\varphi_1)^{1/2}]/2(K^\varphi)^2\varphi_1 \tag{18}$$

$$\varphi^\circ_{A_1} = [2K^\varphi + 1 - (1 + 4K^\varphi)^{1/2}]/2(K^\varphi)^2. \tag{19}$$

$1/S$ and $1/S^\circ$ are, respectively, expressed by

$$1/S = \varphi_{A_1}/r_1\,(1 - K^\varphi\,\varphi_{A_1}) + \varphi_2/r_2 + \varphi_3/r_3 \tag{20}$$

$$1/S^\circ = \varphi^\circ_{A_1}/r_1\,(1 - K^\varphi\,\varphi^\circ_{A_1})\,. \tag{21}$$

We may define K^θ in terms of the surface fraction in the same way as K^φ.

$$K^\theta = (\theta_{A_i}/\theta_{A_1}\,\theta_{A_{i-1}})\,(i-1)/i\,. \tag{22}$$

Dividing Eq. (22) by Eq. (17) gives

$$K^\theta/K^\varphi = [\theta_{A_i}/(\theta_{A_1}\,\theta_{A_{i-1}})]\,[\varphi_{A_i}/(\varphi_{A_1}/\varphi_{A_{i-1}})]^{-1} = \varphi_{A_1}/\theta_{A_1} = \varphi_1/\theta_1 \tag{23}$$

Eq. (23) suggests $\lim_{x_1 \to 1} \varphi_{A_1}/\theta_{A_1} = \varphi^\circ_{A_1}/\theta^\circ_{A_1} = 1$.

The Mecke-Kempter Model. KEHIAIAN and TRESZCZANOWICZ [11] presented detailed discussions on the Mecke-Kempter model. The results are summarized below.

$$K^\varphi = \varphi_{A_i}/(\varphi_{A_1}\,\varphi_{A_{i-1}}) \tag{24}$$

$$\varphi_{A_1} = \varphi_1/(1 + K^\varphi\,\varphi_1) \tag{25}$$

$$\varphi^\circ_{A_1} = 1/(1 + K^\varphi) \tag{26}$$

$$1/S = -\ln\,(1 - K^\varphi\,\varphi_{A_1})/r_1 K^\varphi + \varphi_2/r_2 + \varphi_3/r_3 \tag{27}$$

$$1/S^\circ = -\ln\,(1 - K^\varphi\,\varphi^\circ_{A_1})/r_1\,K^\varphi. \tag{28}$$

The physical (= residual) contribution term of the solution is expressed by Eq. (29) (see Appendix 2).

$$g^E\,(\text{physical})/RT = -\left(\sum_i^3 q_i x_i \ln \sum_j^3 \theta_j \tau_{ji}\right) \tag{29}$$

which gives, when differentiated,

$$\ln\,(\gamma_i)_{\text{phys}} = -q_i \ln\left(\sum_j^3 \theta_j \tau_{ji}\right) + q_i - q_i \sum_j^3 \frac{\theta_j \tau_{ij}}{\sum_j^3 \theta_k \tau_{kj}}\,. \tag{30}$$

The activity coefficient of component i is obtained by

$$\ln \gamma_i = \ln\,(\gamma_i)_{\text{chem}} + \ln\,(\gamma_i)_{\text{phys}}\,. \tag{31}$$

Excess Enthalpy

The excess enthalpy is given as the sum of two contribution terms: the one is chemical and the other physical.

$$h^E = h^E_{\text{chem}} + h^E_{\text{phys}}. \tag{32}$$

Expressions of the chemical contribution term for two models are available elsewhere [12, 13].

For the Kretschmer-Wiebe model, KEHIAIAN and TRESZCZANOWICZ [12] derived

$$h^E_{\text{chem}} = h^\circ x_1 K^\varphi (\varphi_{A_1} - \varphi^\circ_{A_1}) \tag{33}$$

where h° is the enthalpy of hydrogen bond formation.

For the Mecke-Kempter model, TRESZCZANOWICZ [13] presented

$$h^E_{\text{chem}} = h^\circ x_1 [\ln (1 + K^\varphi)/K^\varphi - \ln(1 + K^\varphi \varphi_1)/K^\varphi \varphi_1]. \tag{34}$$

The physical term is given by applying the Gibbs-Helmholtz relation to Eq. (29).

$$h^E_{\text{phys}} = \frac{\partial (g^E_{\text{phys}}/T)}{\partial (1/T)} = -R \sum_i^3 q_i x_i \frac{\sum_j^3 \theta_j \frac{\partial \tau_{ji}}{\partial (1/T)}}{\sum_j^3 \theta_j \tau_{ji}}. \tag{35}$$

3. Data reduction

ABRAMS and PRAUSNITZ [6] suggested that the structural parameters r and q are, respectively, the van der Waals volume and area of the molecule relative to a standard segment.

$$r_i = v_i/v^* \tag{36}$$

$$q_i = a_i/a^* \tag{37}$$

where v^* and a^* are the normalization factors which are connected with the van der Waals volume and area of the standard segment.

VERA *et al.* [9] obtained a linear relation between a_i and v_i as calculated by BONDI [14] over many branched or unbranched chain molecules including alkanes, alcohols, aldehydes, ketones, nitriles, and esters.

$$a_i = k_1 v_i + k_2 \tag{38}$$

$$k_1 = \frac{Z-2}{Z} \frac{a^*}{v^*} = 1.323 \times 10^8 \text{ cm}^{-1} \tag{39}$$

$$k_2 = 2a^*/Z = 6.259 \times 10^8 \text{ cm}^2/\text{mol}. \tag{40}$$

For the assumed value of $Z = 10$, a^* is obtained from Eq. (40) and then v^* from Eq. (39).

Combining Eqs. (38—40) gives

$$Zq_i = 0.4228\, v_i + 2\,. \tag{41}$$

To include molecules with more complex geometry, VERA *et al.* [9] presented a generalizing equation for molecules of any size and shape by introducing the bulk factor l_i.

$$Zq_i = 0.4228\, v_i + 2(1 - l_i)\,. \tag{42}$$

For open chain molecules, branched or unbranched, $l_i = 0$ according to GUGGENHEIM [7]. For cyclic molecules, VERA *et al.* [9] suggested $l_i = 1$. These rules are not retained by the structural parameters which are obtained in accordance with the method of ABRAMS and PRAUSNITZ [6]. We follow the method of VERA *et al.* [9]. Table 1 lists the values of r and q for pure components. We used only the single value of $h^\circ = -6$ kcal/mol for all alcohols as proposed by RENON and PRAUSNITZ [2]. This value fixes the temperature dependence of the chemical equilibrium constant according to the van't Hoff equation.

$$\frac{\partial \ln K^\varphi}{\partial (1/T)} = -\frac{h^\circ}{R}\,. \tag{43}$$

Table 2 shows the chemical equilibrium constants for alcohols at 50 °C. Those values were obtained by considering all data for binary alcohol

Table 1. *Values of the pure component structure parameters*

Component	r	q	l	Component	r	q	l
Methanol	1.15	1.12	0	*n*-Hexane	3.61	3.09	0
Ethanol	1.69	1.55	0	*n*-Heptane	4.15	3.52	0
1-Propanol	2.23	1.98	0	2,2,4-Trimethyl-pentane	4.51	3.81	0
2-Propanol	2.23	1.98	0	*n*-Tetradecane	7.93	6.55	0
1-Butanol	2.77	2.42	0	Cyclopentane	2.64	2.11	1
Cyclopentanol	2.88	2.30	1	Cyclohexane	3.18	2.55	1
Cyclohexanol	3.43	2.74	1	Methylcyclohexane	3.72	2.98	1

Table 2. *Values of the chemical equilibrium constants at 50° C*

Alcohol	Chemical equilibrium constants	
	Kretschmer-Wiebe	Mecke-Kempter
Methanol	280	350
Ethanol	170	170
1-Propanol	90	110
2-Propanol	60	85
1-Butanol	80	95
Cyclopentanol	80	80
Cyclohexanol	70	70

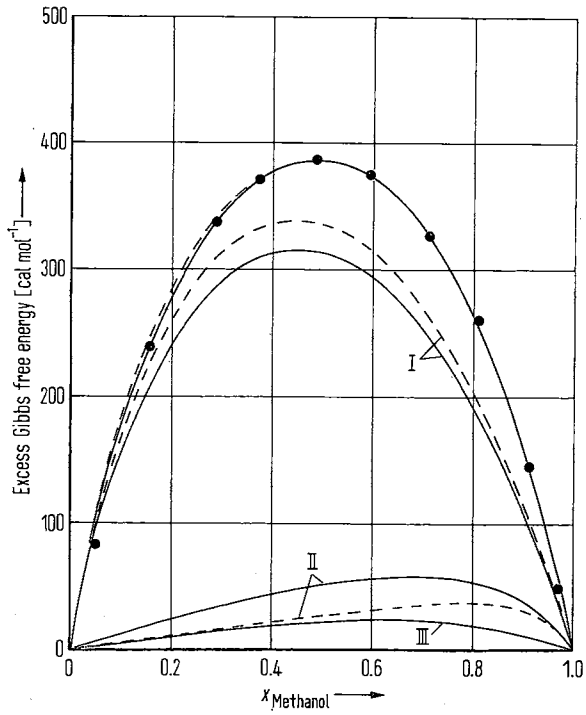

Fig. 1. g^E vs. liquid mole fraction diagram for the methanol-cyclohexane system at 55°C: ● experimental data of MARINICHEV and SUSAREV [15]; ——— calculated by the Kretschmer-Wiebe model; — — — calculated by the Mecke-Kempter model:

I. $\sum_i^2 x_i \ln(\varphi_i/x_i)$; II. $(Z/2)\sum_i^2 q_i x_i \ln(\theta_i/\varphi_i)$; III. $-\sum_i^2 q_i x_i \ln\left(\sum_j^2 \theta_j \tau_{ji}\right)$.

Table 3. *Calculated results for binary*

System (1—2)	Temp. °C	No. of data points	g^E or h^E
Methanol-*n*-hexane [17]	45	9	g^E
Methanol-*n*-hexane [18]	45	17	h^E
Methanol-cyclohexane [15]	55	10	g^E
Ethanol-*n*-hexane [19]	55	9	g^E
Ethanol-cyclohexane [20]	20	7	g^E
Ethanol-cyclohexane [21]	20	5	h^E
Ethanol-cyclohexane [22]	25	21	h^E
Ethanol-methylcyclohexane [23]	35	8	g^E
Ethanol-methylcyclohexane [24]	25	11	h^E
Ethanol-*n*-heptane [25]	20	4	g^E
Ethanol-*n*-heptane [26]	10	21	h^E
Ethanol-*n*-heptane [21]	20	5	h^E
Ethanol-2,2,4-trimethylpentane [27]	50	13	g^E
Ethanol-2,2,4-trimethylpentane [28]	25	7	h^E
1-Propanol-*n*-heptane [29]	60	19	g^E
1-Propanol-*n*-heptane [30]	45	18	h^E
1-Propanol-*n*-tetradecane [31]	30	15	h^E
2-Propanol-*n*-heptane [29]	60	18	g^E
2-Propanol-*n*-heptane [29]	30	26	h^E
1-Butanol-*n*-hexane [32]	25	8	h^E
Cyclopentanol-cyclopentane [33]	25	14	g^E
Cyclopentanol-cyclohexane [34]	25	20	g^E
Cyclopentanol-cyclohexane [34]	25	25	h^E
Cyclohexanol-cyclopentane [34]	25	19	g^E
Cyclohexanol-cyclopentane [34]	25	17	h^E
Cyclohexanol-cyclohexane [33]	25	23	g^E
Cyclohexanol-cyclohexane [35]	25	33	h^E
Cyclohexane-*n*-heptane [21]	20	3	g^E
Cyclohexane-*n*-heptane [21]	20	5	h^E

[a] I = the Kretschmer-Wiebe model

solutions. Figure 1 illustrates the magnitude of each contribution term to the excess Gibbs free energy data of the methanol-cyclohexane system [15] at 55 °C. The $(Z/2)\sum_i^2 q_i x_i \ln(\theta_i/\varphi_i)$ term becomes appreciable in methanol solutions and it is negligible in other alcohol so-

systems based on the Kretschmer-Wiebe model

Abs. arith. mean deviation (cal mol^{-1})		Values of parameters in the Kretschmer-Wiebe model			
		C_1	C_2	D_1	D_2
I[a]	II[b]	(cal mol^{-1})		(cal mol^{-1} K^{-1})	
4.2	7.4	−215.35	478.62		
6.3	0.7	− 84.49	496.25	0.2876	0.1247
4.3	6.1	−257.71	539.63		
6.4	6.7	393.49	−246.00		
3.9	5.0	− 51.71	168.59		
0.8	0.7	152.57	920.17	0.5080	2.2557
1.0	0.5	−307.39	555.98	−1.3199	1.7184
1.6	2.7	− 33.81	114.58		
2.9	1.8	153.85	458.40	0.9416	0.7517
1.3	2.9	−177.40	345.67		
3.1	1.7	−123.67	356.88	0.3864	0.2693
0.9	1.7	42.51	406.96	0.6188	0.5242
3.1	4.2	− 35.05	110.80		
3.2	2.3	88.16	495.95	0.2603	1.6149
2.5	3.7	−115.72	208.64		
3.6	2.8	2657.59	1350.03	6.1106	4.2752
1.8	2.8	159.92	31.31	1.9268	−1.0742
3.5	5.7	−117.18	193.24		
4.0	3.9	− 93.22	239.38	−0.0941	0.2509
2.6	2.6	179.02	593.21	0.5385	2.2236
1.7	2.5	−236.98	447.60		
1.9	2.9	−261.45	445.84		
3.2	4.4	37.09	93.37	0.0341	0.0666
2.2	2.9	−205.31	403.34		
3.8	5.5	80.35	43.48	0.0200	0.0983
2.0	2.7	−216.44	375.35		
1.7	2.5	70.74	485.83	−0.2968	2.1437
0.3		− 22.15	40.72		
0.3		− 94.80	153.34	−0.1599	−0.0295

[b] II = the Mecke-Kempter model

lutions. In fitting the excess enthalpy data, we assumed that the energy parameters change with temperature linearly.

$$u_{ji} - u_{ii} = C_i + D_i (T - 273.15). \tag{44}$$

The simplex method developed by NELDER and MEAD [16] was used to obtain the constants C_i and D_i. Tables 3 and 4 present, re-

Table 4. *Calculated results for binary systems based on the Mecke-Kempter model*

System (1 — 2)	Temp. °C	No. of data points	g^E or h^E	Abs. arith. mean deviation (cal mol^{-1})	C_1 (cal mol^{-1})	C_2 (cal mol^{-1})	D_1 (cal mol^{-1} K^{-1})	D_2 (cal mol^{-1} K^{-1})
Methanol-*n*-hexane [17]	45	9	g^E	7.4	— 410.08	852.58		
Methanol-*n*-hexane [18]	45	17	h^E	0.7	3348.81	451.58	5.5918	0.3845
Methanol-cyclohexane [15]	55	10	g^E	6.1	— 435.90	871.52		
Ethanol-*n*-hexane [19]	55	9	g^E	6.7	181.31	—127.62		
Ethanol-cyclohexane [20]	20	7	g^E	5.0	— 201.48	350.90		
Ethanol-cyclohexane [21]	20	5	h^E	0.7	67.79	176.81	0.1259	0.0117
Ethanol-cyclohexane [22]	25	21	h^E	0.5	35.31	142.26	0.1235	—0.2352
Ethanol-methylcyclohexane [23]	35	8	g^E	2.7	— 291.14	953.96		
Ethanol-methylcyclohexane [24]	25	11	h^E	1.8	— 186.34	331.93	—0.1919	0.2521
Ethanol-*n*-heptane [25]	20	4	g^E	2.9	— 33.84	630.14		
Ethanol-*n*-heptane [26]	10	21	h^E	1.7	— 26.00	221.36	0.0754	0.0730
Ethanol-*n*-heptane [21]	20	5	h^E	1.7	— 39.24	189.84	0.0684	—0.0819
Ethanol-2,2,4-trimethylpentane [27]	50	13	g^E	4.2	— 281.21	416.52		
Ethanol-2,2,4-trimethylpentane [28]	25	7	h^E	2.3	128.01	37.69	0.0609	0.0843
1-Propanol-*n*-heptane [29]	60	19	g^E	3.7	— 325.24	491.46		
1-Propanol-*n*-heptane [30]	45	18	h^E	2.8	56.30	601.90	—0.2510	2.2913
1-Propanol-*n*-tetradecane [31]	30	15	h^E	2.8	410.00	—255.06		
2-Propanol-*n*-heptane [29]	60	18	g^E	5.7	— 396.41	598.98		
2-Propanol-*n*-heptane [29]	30	26	h^E	3.9	68.76	147.68	0.1156	0.1204
1-Butanol-*n*-hexane [32]	25	8	h^E	2.6	171.00	— 32.43	0.1044	0.0389
Cyclopentanol-cyclopentane [33]	25	14	g^E	2.5	— 301.75	547.34		
Cyclopentanol-cyclohexane [34]	25	20	g^E	2.9	— 342.54	582.56		
Cyclopentanol-cyclohexane [34]	25	25	h^E	4.4	39.61	115.90	0.0284	0.0234
Cyclohexanol-cyclopentane [34]	25	19	g^E	2.9	— 266.31	492.48		
Cyclohexanol-cyclopentane [34]	25	17	h^E	5.5	75.89	85.86	0.0684	0.0816
Cyclohexanol-cyclohexane [33]	25	23	g^E	2.7	— 282.84	474.13		
Cyclohexanol-cyclohexane [35]	25	33	h^E	2.5	— 171.86	218.99	—3.2852	4.6084

Table 5. Comparison of predicted results of the excess Gibbs free energy and excess enthalpy for the ethanol-cyclohexane-n-heptane system at 20 °C

Mole fraction		Exptl. g^E	Deviation of calculated values from experimental data Δ [a] (cal mol^{-1})					
		(cal mol^{-1})	Kretschmer-Wiebe			Mecke-Kempter		
x_1	x_2		I [b]	II [c]	III [d]	I	II [e]	III [e]
0.3303	0.3204	315.6	−1.0	3.8	−5.1	−1.8	−5.1	−7.0
0.5978	0.2019	317.0	1.4	4.0	−0.5	3.0	−1.6	3.2
0.2534	0.3957	286.0	−0.1	5.1	−4.0	−2.1	−2.5	−7.0
0.2003	0.6006	250.8	−2.6	2.1	−6.0	−5.4	−0.6	−9.0
0.4059	0.1962	332.3	−0.9	2.6	−4.6	−0.4	−10.5	−5.6
0.3997	0.4013	327.3	−2.0	2.7	−6.0	−1.9	0.8	−5.5
0.2046	0.1997	257.4	0.7	3.9	−2.9	−1.9	−8.8	−7.5
Abs. arith. mean dev.			1.2	3.4	4.1	2.4	4.3	6.9
Mole fraction		Exptl. h^E						
x_1	x_2	(cal mol^{-1})	I	II	III	I	II	III
0.3303	0.3204	166.7	−0.8	5.6	−5.1	0.6	1.7	−0.2
0.5978	0.2019	142.1	0.0	3.4	2.9	−1.1	−0.1	−1.6
0.2534	0.3957	166.8	−1.6	4.9	−5.0	0.0	1.8	0.6
0.2003	0.6006	157.3	−1.7	3.3	−1.2	−0.5	1.6	4.0
0.4059	0.1962	158.2	0.1	5.4	−4.6	0.6	1.0	−1.4
0.3997	0.4013	164.6	−0.7	4.2	−2.5	−0.1	0.5	0.3
0.2046	0.1997	148.8	−1.1	3.7	−7.0	−0.6	1.3	−2.0
Abs. arith. mean dev.			0.9	4.3	4.1	0.5	1.1	1.4

[a] Δ = Experimental value − calculated value.
[b] I = New equation.
[c] II = Nonathermal Flory-Huggins equation having a new physical term. Cited from NAGATA [4].
[d] III = Conventional nonathermal Flory-Huggins equation. Cited from NAGATA [37].
[e] II, III = Cited from NAGATA [5].

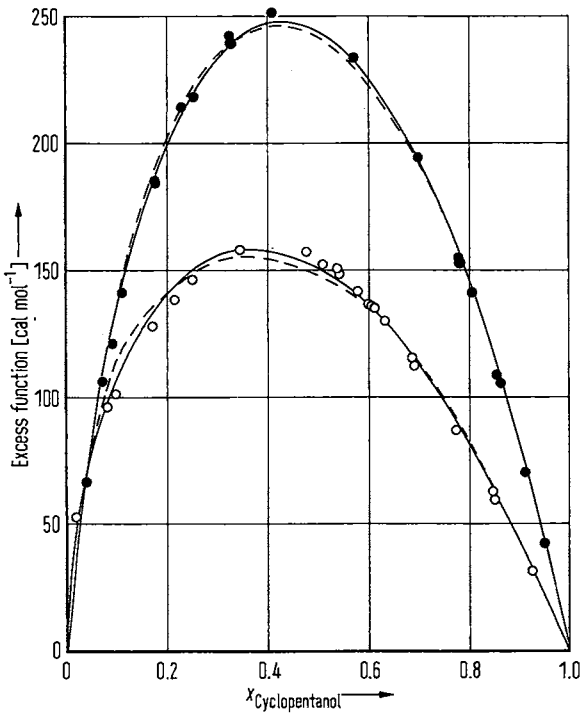

Fig. 2. Excess functions for the cyclopentanol-cyclohexane system at 25°C: ● experimental g^E data of BENSON *et al.* [34]; ○ experimental h^E data of BENSON *et al.* [34]; ——— calculated by the Kretschmer-Wiebe model; — — — calculated by the Mecke-Kempter model

spectively, calculated results for binary systems based on the Kretschmer-Wiebe and the Mecke-Kempter models. The goodness of fit is about the same for the two models. BECKER *et al.* [36] presented the results of least-squares fit of their models with chain association of one component to the excess Gibbs free energy data on cycloalkanol-cycloalkane systems [33, 34] and found a good approximation of the concentration dependence of self-association. We applied the present theory to represent the excess properties for cycloalkanol-cycloalkane systems [33—35]. Tentatively we assumed $h^\circ = -6$ kcal/mol as the enthalpy of hydrogen bond formation of cycloalkanols. Figures 2 and 3 show that the calculated results are in good agreement with the experimental data of these two systems.

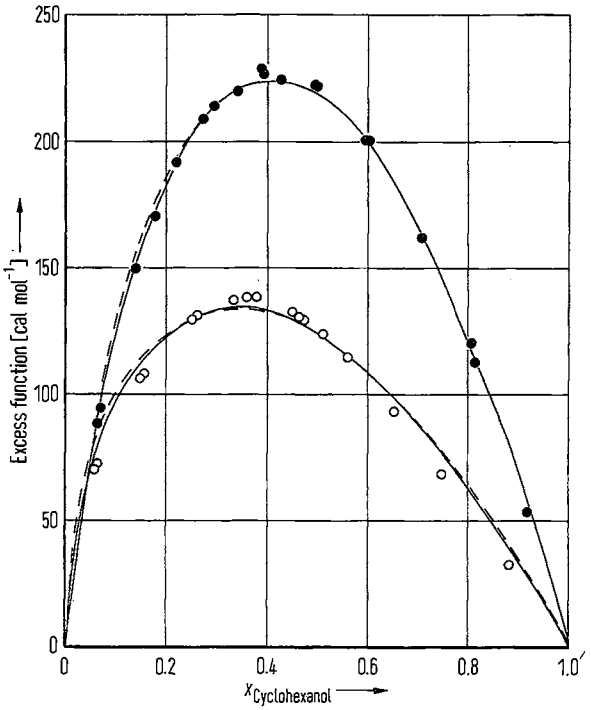

Fig. 3. Excess functions for the cyclohexanol-cyclopentane system at 25 °C: ● experimental g^E data of BENSON *et al.* [34]; ○ experimental h^E data of BENSON *et al.* [34]; ——— calculated by the Kretschmer-Wiebe model; — — — calculated by the Mecke-Kempter model

Table 5 lists a comparison of calculated and experimental values for the excess thermodynamic functions of the ethanol-cyclohexane-*n*-heptane system [21] at 20 °C. The calculated results were obtained from the binary parameters given in Tables 3 and 4. The present theory seems to have a better predictive ability than the previous equations [4, 5, 37] for the two association models.

Our forthcoming paper will be concerned with the extension of the present theory to alcohol-nonassociating active component systems.

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Appendix 1

$$\sum_j^{\infty} \varphi_{A_j}(l_1 - r_1 l_{A_j}/r_{A_j}) + \varphi_2(l_1 - r_1 l_2/r_2) + \varphi_3(l_1 - r_1 l_3/r_3)$$
$$- \sum_j^{\infty} \varphi^{\circ}_{A_j}(l_1 - r_1 l_{A_j}/r_{A_j})$$
$$= - r_1 \left[\sum_j^{\infty} \varphi_{A_j}(l_{A_j} - 1 + 1)/r_{A_j} + \varphi_2(l_2 - 1 + 1)/r_2 + \varphi_3(l_3 - 1 + 1)/r_3 \right]$$
$$+ r_1 \sum_j^{\infty} \varphi^{\circ}_{A_j}(l_{A_j} - 1 + 1)/r_{A_j} + l_1 \left(\sum_j^{\infty} \varphi_{A_j} + \varphi_2 + \varphi_3 - \sum_j^{\infty} \varphi^{\circ}_{A_j} \right)$$
$$= r_1 \left[\sum_j^{\infty} \varphi_{A_j}(1 - l_{A_j})/r_{A_j} + \varphi_2(1 - l_2)/r_2 + \varphi_3(1 - l_3)/r_3 \right]$$
$$- r_1 \left(\sum_j^{\infty} \varphi_{A_j}/r_{A_j} + \varphi_2/r_2 + \varphi_3/r_3 \right)$$
$$- r_1 \sum_j^{\infty} \varphi_{A_j}(1 - l_{A_j})/r_{A_j} + r_1 \sum_j^{\infty} \varphi^{\circ}_{A_j}/r_{A_j}$$
$$= r_1 [\varphi_1(1 - l_1)/r_1 + \varphi_2(1 - l_2)/r_2 + \varphi_3(1 - l_3)/r_3]$$
$$- r_1/S + r_1/S^{\circ} + l_1 - 1 \qquad \text{(A 1)}$$

where

$$1/S = \sum_j^{\infty} \varphi_{A_j}/r_{A_j} + \varphi_2/r_2 + \varphi_3/r_3 \qquad \text{(A 2)}$$

$$1/S^{\circ} = \sum_j^{\infty} \varphi^{\circ}_{A_j}/r_{A_j}. \qquad \text{(A 3)}$$

Appendix 2

The physical contribution term of a multicomponent system of the chemical species $A_1, A_2, \ldots A_n$ and inert components (2 and 3) is expressed by Eq. (3).

$$g^E(\text{physical})/RT = - \sum_i^{\infty} q_{A_i} x_{A_i} \ln \left(\theta_2 \tau_{2A_i} + \theta_3 \tau_{3A_i} + \sum_j^{\infty} \theta_{A_j} \tau_{A_i A_j} \right)$$
$$- q_2 x_2 \ln \left(\theta_2 + \theta_3 \tau_{32} + \sum_i^{\infty} \theta_{A_i} \tau_{A_i 2} \right)$$
$$- q_3 x_3 \ln \left(\theta_2 \tau_{23} + \theta_3 + \sum_i^{\infty} \theta_{A_i} \tau_{A_i 3} \right). \qquad \text{(A 4)}$$

We assume that $\tau_{A_i A_j}$, $\tau_{A_i 2}$, and $\tau_{A_i 3}$ are independent of the subscripts i and j. Recalling that

$$\sum_i^\infty \theta_{A_i} = \theta_1, \text{ and } \sum_i^\infty q_{A_i} x_{A_i} = q_1 \sum_i^\infty i x_{A_i} = q_1 x_1,$$

we obtain

$$\begin{aligned} g^E(\text{physical})/RT = & -q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21} + \theta_3 \tau_{31}) \\ & - q_2 x_2 \ln(\theta_1 \tau_{12} + \theta_2 + \theta_3 \tau_{32}) \\ & - q_3 x_3 \ln(\theta_1 \tau_{13} + \theta_2 \tau_{23} + \theta_3) \\ = & -\sum_i^3 q_i x_i \ln\left(\sum_j^3 \theta_j \tau_{ji}\right), \end{aligned} \tag{A5}$$

where

$$\tau_{ji} = \exp[-(u_{ji} - u_{ii})/RT]. \tag{A6}$$

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